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Applicant(s) : Dai Nippon Printing Co., Ltd.

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[INVENTOR]	
[DOMICILE OR RESIDENCE]	c/o Dai Nippon Printing Co., Ltd. 1-1, Ichigaya Kagacho 1-chome, Shinjuku-ku, Tokyo
[NAME]	Yagi Hiroshi
[INVENTOR]	
[DOMICILE OR RESIDENCE]	c/o Dai Nippon Printing Co., Ltd. 1-1, Ichigaya Kagacho 1-chome, Shinjuku-ku, Tokyo
[NAME]	Kihara Takeshi
[INVENTOR]	
[DOMICILE OR RESIDENCE]	c/o Dai Nippon Printing Co., Ltd. 1-1, Ichigaya Kagacho 1-chome, Shinjuku-ku, Tokyo
[NAME]	Suzuki Koichi
[APPLICANT]	
[ID NUMBER]	000002897

[NAME]	Dai Nippon Printing Co., Ltd.	
[REPRESENTATIVE]	Kitajima Yoshitoshi	
[AGENT]		
[ID NUMBER]	100095463	
[PATENT ATTORNEY]		
[NAME]	Yoneda Junzo	
[Telephone Number]	03-3255-7888	
[AGENT]		
[ID NUMBER]	100098006	
[PATENT ATTORNEY]		
[NAME]	Sarada Hideo	
[Telephone Number]	03-3255-7888	
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[NAME OF DOCUMENT]      Claim

[Claim 1]

A microreactor for obtaining hydrogen gas by reforming a feed material, characterized by comprising:

a joined body comprising a metal substrate provided with a microchannel portion on one surface thereof, and a metal cover member having a feed material inlet and a gas outlet and joined to said metal substrate so as to cover said microchannel portion, a flow path formed by said microchannel portion located inside said joined body and said metal cover member, and a catalyst supported on a whole inner wall surface of said flow path.

[Claim 2]

A microreactor according to claim 1, wherein said flow path has no angular portion on the inner wall surface along a fluid flow direction.

[Claim 3]

A microreactor according to claim 1 or 2, wherein the catalyst is supported on the inner wall surface of said flow path via a metal oxide film.

[Claim 4]

A microreactor according to claim 3, wherein said metal oxide film is formed by anodic oxidation of said metal substrate and said metal cover member.

[Claim 5]

A microreactor according to claim 3, wherein said metal oxide film is formed by a boehmite treatment.

[Claim 6]

A microreactor according to any of claims 1 to 5, wherein said metal substrate is provided with a heater on a surface opposite to the surface where said microchannel portion is formed, via an insulating film.

[Claim 7]

A microreactor for obtaining hydrogen gas by reforming a feed material, characterized by comprising:

a joined body formed by joining together a pair of metal substrates each having a microchannel portion on one surface thereof and having patterns of said microchannel portions that are in a plane symmetrical relationship to each other, such that said microchannel portions confront each other, a flow path formed by said microchannel portions confronting each other inside said joined body, a catalyst supported on a whole inner wall surface of said flow path, a feed material inlet located at one end portion of said flow path, and a gas outlet located at the other end portion of said flow path.

[Claim 8]

A microreactor according to claim 7, wherein said flow path has no angular portion on the inner wall surface along a fluid flow direction, and the shape of the inner wall surface in a section perpendicular to the flow direction of the flow path is generally circular or oval.

[Claim 9]

A microreactor according to claim 7 or 8, wherein

the catalyst is supported on the inner wall surface of said flow path via a metal oxide film.

[Claim 10]

A microreactor according to claim 9, wherein said metal oxide film is formed by anodic oxidation of said metal substrates.

[Claim 11]

A microreactor according to claim 9, wherein said metal oxide film is formed by a boehmite treatment.

[Claim 12]

A microreactor according to any of claims 7 to 11, wherein at least one of said metal substrates is provided with a heater on a surface opposite to the surface where said microchannel portion is formed, via an insulating film.

[Claim 13]

A production method of a microreactor for obtaining hydrogen gas by reforming a feed material, characterized by comprising:

a channel portion forming step of forming a microchannel portion on one surface of a metal substrate;

a joining step of joining a metal cover member having a feed material inlet and a gas outlet to said metal substrate so as to cover said microchannel portion to thereby form a joined body having a flow path;

a surface processing step of forming a metal oxide film on an inner wall surface of said flow path; and

a catalyst applying step of applying a catalyst to

the inner wall surface of said flow path via said metal oxide film.

[Claim 14]

A production method of a microreactor according to claim 13, wherein said surface processing step forms said metal oxide film by anodically oxidizing said metal substrate and said metal cover member.

[Claim 15]

A production method of a microreactor according to claim 13, wherein said surface processing step forms said metal oxide film by a boehmite treatment.

[Claim 16]

A production method of a microreactor for obtaining hydrogen gas by reforming a feed material, characterized by comprising:

a channel portion forming step of forming microchannel portions with patterns that are plane-symmetrical with each other, on either surfaces of a pair of metal substrates;

a joining step of joining together said pair of metal substrates so that said microchannel portions confront each other, to thereby form a joined body having a flow path;

a surface processing step of forming a metal oxide film on an inner wall surface of said flow path; and

a catalyst applying step of applying a catalyst to the inner wall surface of said flow path via said metal

oxide film.

[Claim 17]

A production method of a microreactor according to claim 16, wherein said surface processing step forms said metal oxide film by anodically oxidizing said metal substrates.

[Claim 18]

A production method of a microreactor according to claim 16, wherein said surface processing step forms said metal oxide film by a boehmite treatment.

[Claim 19]

A production method of a microreactor according to any of claims 13 to 18, wherein said channel portion forming step forms said microchannel portion on each metal substrate such that a section thereof becomes U-shaped or semicircular, and no angular portion exists on a wall surface along a flow direction.

[Claim 20]

A production method of a microreactor according to any of claims 13 to 19, wherein said catalyst applying step fills the flow path of said joined body with a catalyst suspension, then removes said catalyst suspension and dries the inside of the flow path.

[Claim 21]

A production method of a microreactor according to claim 20, wherein said catalyst applying step gives vibration or rotation to said joined body upon drying.

[NAME OF DOCUMENT]      Specification

[TITLE OF THE INVENTION]   Microreactor for Hydrogen  
Production and Production Method Thereof

[TECHNICAL FIELD]

[0001]

The present invention relates to a microreactor for use in a reformer for hydrogen production and, in particular, to a microreactor for obtaining hydrogen gas by reforming a feed material such as methanol, and a production method of such a microreactor.

[BACKGROUND ART]

[0002]

In recent years, attention has been paid to using hydrogen as fuel because of no generation of global warming gas such as carbon dioxide in terms of the global environmental protection, and of the high energy efficiency. Particularly, attention has been paid to fuel cells because they can directly convert hydrogen to electric power and enable the high energy conversion efficiency in the cogeneration system utilizing generated heat. The fuel cells have been hitherto employed under the particular conditions such as in the space development and the ocean development. Recently, however, the development has advanced toward using them for automobile and household distributed power supplies, and fuel cells for portable devices have also been developed.

Among the fuel cells, the fuel cell for producing

electricity by electrochemically reacting hydrogen gas obtained by reforming hydrocarbon fuel such as natural gas, gasoline, butane gas, or methanol, and oxygen in air is composed of a reformer for producing hydrogen gas by, in general, steam reforming hydrocarbon fuel, a fuel cell body for producing electricity, and so forth.

[0003]

In the reformer for obtaining hydrogen gas by steam reforming methanol or the like as a feed material, a Cu-Zn catalyst is mainly used to carry out steam reforming of the feed material by an endothermic reaction. In the industrial fuel cell, since the startup and stop are not frequently carried out, a temperature fluctuation of the reformer is not liable to occur. However, in the fuel cell for automobile or portable device, since the startup and stop are carried out frequently, the reformer is required to rise up quickly (a time for reaching a steam reforming temperature of methanol is short) upon starting up from the stopped state.

On the other hand, particularly for the portable device, reduction in size of the fuel cell is essential so that reduction in size of the reformer has been studied variously. For example, there has been developed a microreactor having a silicon substrate or a ceramic substrate formed with a microchannel portion and carrying a catalyst in this microchannel portion (Patent Document 1).

[PATENT DOCUMENT 1]      Laid-open Unexamined Patent

Publication No. 2002-252014

[DISCLOSURE OF THE INVENTION]

[PROBLEM TO BE SOLVED BY THE INVENTION]

[0004]

In the conventional microreactor, however, there has been a problem that the heat utilization efficiency is low so that the rising speed of the reformer is slow upon starting up from the stopped state. There has also been a problem that processing by a micromachine, etc. are required and therefore the production cost is high. Further, a space allowed for the microreactor is strictly limited in the fuel cell for portable device so that further reduction in size has been strongly demanded.

Further, the conventional microreactor has a low reaction efficiency and therefore a microreactor with a higher reaction efficiency has been demanded. Moreover, in the conventional microreactor, there has also been a problem that there is possibility of a catalyst to be deactivated by heat in the production stage, and therefore, a usable catalyst is limited and the production process management is difficult.

[0005]

Therefore, the present invention has been made for solving the foregoing problems. An object thereof is to provide a microreactor that enables a small-sized and highly-efficient reformer for hydrogen production, and a production method that can easily produce such a

microreactor.

[MEANS FOR SOLVING THE PROBLEM]

[0006]

For accomplishing such an object, the present invention is configured such that a microreactor for obtaining hydrogen gas by reforming a feed material, comprises a joined body comprising a metal substrate provided with a microchannel portion on one surface thereof, and a metal cover member having a feed material inlet and a gas outlet and joined to said metal substrate so as to cover said microchannel portion, a flow path formed by said microchannel portion located inside said joined body and said metal cover member, and a catalyst supported on a whole inner wall surface of said flow path.

[0007]

As another mode of the present invention, it is configured such that said flow path has no angular portion on the inner wall surface along a fluid flow direction.

As another mode of the present invention, it is configured such that the catalyst is supported on the inner wall surface of said flow path via a metal oxide film.

As another mode of the present invention, it is configured such that said metal oxide film is formed by anodic oxidation of said metal substrate and said metal cover member, or that said metal oxide film is formed by a boehmite treatment.

As another mode of the present invention, it is

configured such that said metal substrate is provided with a heater on a surface opposite to the surface where said microchannel portion is formed, via an insulating film.

[0008]

Further, the present invention is configured such that a microreactor for obtaining hydrogen gas by reforming a feed material, comprises a joined body formed by joining together a pair of metal substrates each having a microchannel portion on one surface thereof and having patterns of said microchannel portions that are in a plane symmetrical relationship to each other, such that said microchannel portions confront each other, a flow path formed by said microchannel portions confronting each other inside said joined body, a catalyst supported on a whole inner wall surface of said flow path, a feed material inlet located at one end portion of said flow path, and a gas outlet located at the other end portion of said flow path.

[0009]

As another mode of the present invention, it is configured such that said flow path has no angular portion on the inner wall surface along a fluid flow direction, and the shape of the inner wall surface in a section perpendicular to the flow direction of the flow path is generally circular or oval.

As another mode of the present invention, it is configured such that the catalyst is supported on the inner wall surface of said flow path via a metal oxide film.

As another mode of the present invention, it is configured such that said metal oxide film is formed by anodic oxidation of said metal substrates, or that said metal oxide film is formed by a boehmite treatment.

As another mode of the present invention, it is configured such that at least one of said metal substrates is provided with a heater on a surface opposite to the surface where said microchannel portion is formed, via an insulating film.

[0010]

Further, the present invention is configured such that a production method of a microreactor for obtaining hydrogen gas by reforming a feed material, comprises a channel portion forming step of forming a microchannel portion on one surface of a metal substrate; a joining step of joining a metal cover member having a feed material inlet and a gas outlet to said metal substrate so as to cover said microchannel portion to thereby form a joined body having a flow path; a surface processing step of forming a metal oxide film on an inner wall surface of said flow path; and a catalyst applying step of applying a catalyst to the inner wall surface of said flow path via said metal oxide film.

As another mode of the present invention, it is configured such that said surface processing step forms said metal oxide film by anodically oxidizing said metal substrate and said metal cover member, or that said surface

processing step forms said metal oxide film by a boehmite treatment.

[0011]

Further, the present invention is configured such that a production method of a microreactor for obtaining hydrogen gas by reforming a feed material, comprises a channel portion forming step of forming microchannel portions with patterns that are plane-symmetrical with each other, on either surfaces of a pair of metal substrates; a joining step of joining together said pair of metal substrates so that said microchannel portions confront each other, to thereby form a joined body having a flow path; a surface processing step of forming a metal oxide film on an inner wall surface of said flow path; and a catalyst applying step of applying a catalyst to the inner wall surface of said flow path via said metal oxide film.

[0012]

As another mode of the present invention, it is configured such that said surface processing step forms said metal oxide film by anodically oxidizing said metal substrates, or that said surface processing step forms said metal oxide film by a boehmite treatment.

As another mode of the present invention, it is configured such that said channel portion forming step forms said microchannel portion on each metal substrate such that a section thereof becomes U-shaped or semicircular, and no angular portion exists on a wall

surface along a flow direction.

As another mode of the present invention, it is configured such that said catalyst applying step fills the flow path of said joined body with a catalyst suspension, then removes said catalyst suspension and dries the inside of the flow path, and further that said catalyst applying step gives vibration or rotation to said joined body upon drying.

#### [ADVANTAGES OF THE INVENTION]

[0013]

According to the foregoing present invention, since the catalyst is supported on the whole inner wall surface of the flow path, the reaction area is increased to thereby improve a reaction efficiency so that effective utilization of a space is made possible. Further, since the metal substrate forming the microreactor has a higher thermal conductivity and a smaller heat capacity as compared with a silicon substrate or a ceramic substrate, heat is transmitted from the heater to the applied catalyst with a high efficiency, so that there is enabled a reformer for hydrogen production wherein the rising is fast upon starting up from the stopped state and the utilization efficiency of the input power to the heater is high.

Further, since the catalyst is applied after the joined body having the flow path therein is formed in the joining process, there is no possibility of deactivation of the catalyst due to heat in the joining process so that the

selection width of the catalyst is broadened. Further, by preparing a plurality of joined bodies through completion up to the joining process and applying desired catalysts to these joined bodies, it is possible to produce microreactors to be used in different reactions, for example, microreactors for reforming methanol and for oxidation of carbon monoxide depending on uses, and therefore, simplification of the production processes is made possible. Further, the formation of the microchannel portion on the metal substrate does not require the processing by a micromachine, but can be easily implemented by a low-priced processing method such as etching, and further, the polishing process is also unnecessary, so that reduction in production cost of the microreactor can be achieved. Further, if it is configured such that no angular portion exists on the inner wall surface of the flow path, dispersion of the applying amount in the catalyst applying process is suppressed so that the catalyst can be uniformly applied.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0014]

Hereinbelow, embodiments of the present invention will be described with reference to the drawings.

#### Microreactor

(First Embodiment)

Fig. 1 is a perspective view showing one embodiment of the microreactor of the present invention,

and Fig. 2 is an enlarged longitudinal sectional view of the microreactor shown in Fig. 1, taken along line A-A. In Figs. 1 and 2, the microreactor 1 of the present invention has a joined body 15 comprising a metal substrate 2 formed with a microchannel portion 3 on one surface 2a thereof, and a metal cover member 4 joined to the surface 2a of the metal substrate 2 so as to cover the microchannel portion 3. Inside the joined body 15, there is formed a flow path 5 composed of the microchannel portion 3 and the metal cover member 4, and a catalyst C is supported on the whole inner wall surface of the flow path 5 via a metal oxide film 6. Further, the foregoing metal cover member 4 is provided with a feed material inlet 4a and a gas outlet 4b which are located at respective end portions of the flow path 5. The foregoing metal oxide film 6 is an insulating film and is also formed on the surfaces of the joined body 15 (a surface 2b and side surfaces 2c of the metal substrate 2 and the surface of the metal cover member 4) apart from the inner wall surface of the flow path 5. Further, a heater 7 is provided on the surface 2b of the metal substrate 2 via the metal oxide film 6 and formed with electrodes 8 and 8, and a heater protective layer 9 having electrode opening portions 9a and 9a for exposing the electrodes 8 and 8 is provided so as to cover the heater 7.

[0015]

Fig. 3 is a perspective view showing the side, where the microchannel portion 3 is formed, of the metal

substrate 2 of the microreactor 1 shown in Fig. 1. As shown in Fig. 3, the microchannel portion 3 is formed so as to turn back by 180 degrees at respective tip portions of comb-shaped ribs 2A and 2B and has a shape that is continuous from an end portion 3a to an end portion 3b while meandering. The shape of an inner wall surface of the microchannel portion 3 in a section perpendicular to a fluid flow direction of the flow path 5 is generally semicircular. Further, the turnback of the flow path at each of the tip portions of the comb-shaped ribs 2A and 2B is rounded with no angular portion. The feed material inlet 4a of the metal cover member 4 is located at the end portion 3a of the microchannel portion 3, and the gas outlet 4b is located at the end portion 3b of the microchannel portion 3.

[0016]

For the metal substrate 2 forming the microreactor 1, there can be used such metal that can form the metal oxide film (insulating film) 6 by anodic oxidation. As such metal, there can be cited, for example, Al, Si, Ta, Nb, V, Bi, Y, W, Mo, Zr, Hf, or the like. Among these metals, particularly Al is preferably used in terms of processing suitability, properties such as a heat capacity and a thermal conductivity, and a unit price. The thickness of the metal substrate 2 can be suitably set taking into account the size of the microreactor 1, properties such as a heat capacity and a thermal conductivity of metal to be

used, the size of the microchannel portion 3 to be formed, and so forth. For example, it can be set within a range of about 50 to 2000 $\mu$ m.

[0017]

The microchannel portion 3 formed on the metal substrate 2 is not limited to the shape as shown in Fig. 3, but can be formed into a desirable shape like one wherein an amount of the catalyst C supported on the microchannel portion 3 increases and the flow path length in which a feed material contacts with the catalyst C is prolonged. Particularly, such a shape of the microchannel portion 3 is preferable wherein an angular portion (e.g. a portion of the internal wall surface that is angularly bent at a position where the direction of the flow path changes) does not exist on the internal wall surface along the fluid flow direction of the flow path 5. Further, the shape of the inner wall surface of the microchannel portion 3 in the section perpendicular to the fluid flow direction of the flow path 5 is preferably a circular arc shape, a semicircular shape, or a U-shape. For example, the depth of such a microchannel portion 3 can be set within a range of about 100 to 1000 $\mu$ m, the width thereof can be set within a range of about 100 to 1000 $\mu$ m, and the flow path length thereof can fall within a range of about 30 to 300mm.

In this embodiment, since the metal oxide film 6 is formed on the inner wall surface of the flow path 5, an applying amount of the catalyst C is increased to enable

stable catalyst applying due to a surface structure of the metal oxide film having microholes.

As the catalyst C, it is possible to use a known catalyst that has conventionally been employed for steam reforming.

[0018]

For the metal cover member 4 forming the microreactor 1, there can be used such metal that can form the metal oxide film (insulating film) 6 by anodic oxidation. As such metal, there can be cited, for example, Al, Si, Ta, Nb, V, Bi, Y, W, Mo, Zr, Hf, or the like. Among these metals, particularly Al is preferably used in terms of processing suitability, properties such as a heat capacity and a thermal conductivity, and a unit price. The thickness of the metal cover member 4 can be suitably set taking into account a material to be used and so forth. For example, it can be set within a range of about 20 to 200 $\mu$ m. The feed material inlet 4a and the gas outlet 4b of the metal cover member 4 are provided so as to be located at both end portions 3a and 3b of the microchannel portion 3 formed on the metal substrate 2.

The formation of the metal oxide film (insulating film) 6 by anodic oxidation on the joined body 15 formed by joining together the metal substrate 2 and the metal cover member 4 can be implemented by, in the state where the joined body 15 is connected to an anode as an external electrode, immersing the joined body 15 in an anode

oxidizing solution so as to confront a cathode and energizing it. The thickness of the metal oxide film (insulating film) 6 can be set within a range of, for example, about 5 to 150 $\mu$ m.

[0019]

The heater 7 forming the microreactor 1 is for supplying heat required for steam heating of the feed material, which is an endothermic reaction, and it is possible to use therefor a material such as carbon paste, nichrome (Ni-Cr alloy), W (tungsten), or Mo (molybdenum). The heater 7 can have a shape like one that is obtained by, for example, drawing around a fine line having a width of about 10 to 200 $\mu$ m over the whole of a region on the metal substrate surface 2b (metal oxide film 6) corresponding to a region where the microchannel portion 3 is formed.

Such a heater 7 is formed with the electrodes 8 and 8 for energization. The electrodes 8 and 8 for energization can be formed using a conductive material such as Au, Ag, Pd, or Pd-Ag.

[0020]

The heater protective layer 9 has the electrode opening portions 9a and 9a for exposing the foregoing electrodes 8 and 8 and is disposed so as to cover the heater 7. The heater protective layer 9 can be formed of, for example, photosensitive polyimide, polyimide varnish, or the like. The thickness of the heater protective layer 9 can be suitably set taking into account a material to be

used and so forth. For example, it can be set within a range of about 2 to 25 $\mu$ m.

[0021]

(Second Embodiment)

Fig. 4 is a longitudinal sectional view, corresponding to Fig. 2, showing another embodiment of the microreactor of the present invention. In Fig. 4, the microreactor 21 of the present invention has a joined body 35 comprising a metal substrate 22 formed with a microchannel portion 23 on one surface 22a thereof, and a metal cover member 24 joined to the surface 22a of the metal substrate 22 so as to cover the microchannel portion 23. Inside the joined body 35, there is formed a flow path 25 composed of the microchannel portion 23 and the metal cover member 24, and a catalyst C is supported on the whole inner wall surface of the flow path 25 via a metal oxide film 26. The foregoing metal cover member 24 is provided with a feed material inlet 24a and a gas outlet 24b which are located at respective end portions of the flow path 25. Further, an insulating film 30 is formed on the surface of the joined body 35 (a surface 22b of the metal substrate 22), and a heater 27 is provided on the insulating film 30. The heater 27 is formed with electrodes 28 and 28, and a heater protective layer 29 having electrode opening portions 29a and 29a for exposing the electrodes 28 and 28 is provided so as to cover the heater 27.

[0022]

For the metal substrate 22 forming such a microreactor 21, it is possible to use a material that can form a metal oxide film through a boehmite treatment of Cu, stainless, Fe, Al, or the like. The thickness of the metal substrate 22 can be suitably set taking into account the size of the microreactor 21, properties such as a heat capacity and a thermal conductivity of metal to be used, the size of the microchannel portion 23 to be formed, and so forth. For example, it can be set within a range of about 50 to 2000 $\mu$ m.

The microchannel portion 23 of the metal substrate 22 can be the same as the microchannel portion 3 of the foregoing embodiment.

For the metal cover member 24 forming the microreactor 21, it is possible to use a material that can form a metal oxide film through a boehmite treatment of Cu, stainless, Fe, Al, or the like. The thickness of the metal cover member 24 can be suitably set taking into account a material to be used and so forth. For example, it can be set within a range of about 20 to 200 $\mu$ m. The feed material inlet 24a and the gas outlet 24b of the metal cover member 24 are provided so as to be located at both end portions of the microchannel portion 23 formed on the metal substrate 22.

[0023]

The formation of the metal oxide film 26 by the boehmite treatment in the flow path 25 of the joined body

35 formed by joining together the metal substrate 22 and the metal cover member 24 can be implemented by, for example, using a suspension with boehmite alumina such as alumina sol being dispersed therein, and pouring the suspension with a fully lowered viscosity into the flow path 25, thereafter, drying it to fix a boehmite coating on the inner surface of the flow path (washcoat process). The metal oxide film 26 formed by such a boehmite treatment is an aluminum oxide thin film, and the thickness thereof can be set within a range of, for example, about 0.5 to 5.0 $\mu$ m.

The insulating film 30 formed on the surface 22b of the metal substrate 22 can be formed of, for example, polyimide, ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ), or the like. The thickness of such an insulating film 30 can be suitably set taking into account properties of a material to be used and so forth. For example, it can be set within a range of about 1 to 30 $\mu$ m.

[0024]

The catalyst C, the heater 27, the electrodes 28 and 28, and the heater protective layer 29 forming the microreactor 21 can be the same as the catalyst C, the heater 7, the electrodes 8 and 8, and the heater protective layer 9 forming the microreactor 1, respectively, and therefore, description thereof is omitted herein.

In the microreactor 1, 31 of the present invention as described above, since the catalyst C is supported on the whole inner wall surface of the flow path 5, 25, the

reaction area is increased to thereby obtain a high reaction efficiency. Further, use is made of the metal substrate 2, 22 and the metal cover member 4, 24 each having a higher thermal conductivity and a smaller heat capacity as compared with a silicon substrate or a ceramic substrate, and therefore, heat is transmitted from the heater 7, 27 to the supported catalyst C with a high efficiency, so that there is enabled a reformer for hydrogen production wherein the rising is fast upon starting up from the stopped state and the utilization efficiency of the input power to the heater is high.

[0025]

(Third Embodiment)

Fig. 5 is a perspective view showing another embodiment of the microreactor of the present invention, and Fig. 6 is an enlarged longitudinal sectional view of the microreactor shown in Fig. 5, taken along line B-B. In Figs. 5 and 6, the microreactor 41 of the present invention has a joined body 55 in which a metal substrate 42 formed with a microchannel portion 43 on one surface 42a thereof, and a metal substrate 44 formed with a microchannel portion 45 on one surface 44a thereof are joined together such that the microchannel portion 43 and the microchannel portion 45 confront each other. Inside the joined body 55, there is formed a flow path 46 composed of the confronting microchannel portions 43 and 45, and a catalyst C is supported on the whole inner wall surface of the flow path

46 via a metal oxide film 47. Further, both end portions of the flow path 46 are exposed at one end surface of the foregoing joined body 55 to form a feed material inlet 46a and a gas outlet 46b, respectively. The foregoing metal oxide film 47 is an insulating film and is also formed on the surfaces of the joined body 55 (a surface 42b and side surfaces 42c of the metal substrate 42, and a surface 44b and side surfaces 44c of the metal substrate 44) apart from the inner wall surface of the flow path 46. Further, a heater 48 is provided on the surface 42b of the metal substrate 42 via the metal oxide film 47 and formed with electrodes 49 and 49, and a heater protective layer 50 having electrode opening portions 50a and 50a for exposing the electrodes 49 and 49 is provided so as to cover the heater 48.

[0026]

Fig. 7 is a perspective view showing the side, where the microchannel portion 43 is formed, of the metal substrate 42 and the side, where the microchannel portion 45 is formed, of the metal substrate 44, of the microreactor 41 shown in Fig. 5. As shown in Fig. 7, the microchannel portion 43 is formed so as to turn back by 180 degrees at respective tip portions of comb-shaped ribs 42A and 42B and has a shape that is continuous from an end portion 43a to an end portion 43b while meandering. The microchannel portion 45 is formed so as to turn back by 180 degrees at respective tip portions of comb-shaped ribs 44A

and 44B and has a shape that is continuous from an end portion 45a to an end portion 45b while meandering. Further, the microchannel portion 43 and the microchannel portion 45 have pattern shapes that are in a symmetrical relationship with respect to a joining plane between the metal substrates 42 and 44. Therefore, by joining together the metal substrates 42 and 44, the end portion 43a of the microchannel portion 43 is located on the end portion 45a of the microchannel portion 45, and the end portion 43b of the microchannel portion 43 is located on the end portion 45b of the microchannel portion 45, so that the microchannel portion 43 and the microchannel portion 45 completely confront each other. The shape of the inner wall surface of the flow path 46 formed by such microchannel portions 43 and 45 is generally circular in a section perpendicular to a fluid flow direction of the flow path 46. Further, the turnback of the flow path 46 at each of the tip portions of the comb-shaped ribs 42A and 42B or the comb-shaped ribs 44A and 44B is rounded with no angular portion. The end portion 43a of the microchannel portion 43 and the end portion 45a of the microchannel portion 45 form the feed material inlet 46a, while the end portion 43b of the microchannel portion 43 and the end portion 45b of the microchannel portion 45 form the gas outlet 46b.

[0027]

For the metal substrate 42, 44 forming the microreactor 41, there can be used such metal that can form

the metal oxide film (insulating film) 47 by anodic oxidation. As such metal, it is possible to use the same one for the metal substrate 2 in the foregoing embodiment. Further, the thickness of the metal substrate 42, 44 can be suitably set taking into account the size of the microreactor 41, properties such as a heat capacity and a thermal conductivity of metal to be used, the size of the microchannel portion 43, 45 to be formed, and so forth. For example, it can be set within a range of about 400 to 1000 $\mu$ m.

[0028]

The microchannel portion 43, 45 formed on the metal substrate 42, 44 is not limited to the shape as shown in Fig. 7, but can be formed into a desirable shape like one wherein an amount of the catalyst C supported on the microchannel portion 43, 45 increases and the flow path length in which a feed material contacts with the catalyst C is prolonged. Particularly, such a shape of the microchannel portion 43, 45 is preferable wherein an angular portion (e.g. a portion of the internal wall surface that is angularly bent at a position where the direction of the flow path changes) does not exist on the internal wall surface along the fluid flow direction of the flow path 46. Further, the shape of the inner wall surface of the microchannel portion 43, 45 in the section perpendicular to the fluid flow direction is preferably a circular arc shape, a semicircular shape, or a U-shape.

Thereby, the shape of the inner wall surface, in the section perpendicular to the fluid flow direction, of the fluid path 46 formed by the microchannel portions 43 and 45 becomes generally circular. For example, the depth of such a microchannel portion 43, 45 can be set within a range of about 100 to 1000 $\mu$ m, the width thereof can be set within a range of about 100 to 1000 $\mu$ m, and the flow path length thereof can fall within a range of about 30 to 300mm.

[0029]

In this embodiment, since the metal oxide film 47 is formed on the inner wall surface of the flow path 46, an applying amount of the catalyst C is increased to enable stable catalyst applying due to a surface structure of the metal oxide film having microholes.

As the catalyst C, it is possible to use a known catalyst that has conventionally been employed for steam reforming.

The formation of the metal oxide film (insulating film) 47 by anodic oxidation on the joined body 55 formed by joining together the metal substrates 42 and 44 can be implemented by, in the state where the joined body 55 is connected to an anode as an external electrode, immersing the joined body 55 in an anode oxidizing solution so as to confront a cathode and energizing it. The thickness of the metal oxide film (insulating film) 47 can be set within a range of, for example, about 5 to 150 $\mu$ m.

The catalyst C, the heater 48, the electrodes 49

and 49, and the heater protective layer 50 forming the microreactor 41 can be the same as the catalyst C, the heater 7, the electrodes 8 and 8, and the heater protective layer 9 forming the microreactor 1, respectively, and therefore, description thereof is omitted herein.

[0030]

(Fourth Embodiment)

Fig. 8 is a longitudinal sectional view, corresponding to Fig. 6, showing another embodiment of the microreactor of the present invention. In Fig. 8, the microreactor 61 of the present invention has a joined body 75 in which a metal substrate 62 formed with a microchannel portion 63 on one surface 62a thereof, and a metal substrate 64 formed with a microchannel portion 65 on one surface 64a thereof are joined together such that the microchannel portion 63 and the microchannel portion 65 confront each other. Inside the joined body 75, there is formed a flow path 66 composed of the confronting microchannel portions 63 and 65, and a catalyst C is supported on the whole inner wall surface of the flow path 66 via a metal oxide film 67. Further, both end portions of the flow path 66 are exposed at one end surface of the foregoing joined body 75 to form a feed material inlet (not illustrated) and a gas outlet (not illustrated), respectively. Further, an insulating film 71 is formed on the surface of the joined body 75 (a surface 62b of the metal substrate 62), and a heater 68 is provided on the

insulating film 71. The heater 68 is formed with electrodes 69 and 69, and a heater protective layer 70 having electrode opening portions 70a and 70a for exposing the electrodes 69 and 69 is provided so as to cover the heater 68.

[0031]

For the metal substrate 62, 64 forming such a microreactor 61, it is possible to use a material that can form a metal oxide film through a boehmite treatment of Cu, stainless, Fe, Al, or the like. The thickness of the metal substrate 62, 64 can be suitably set taking into account the size of the microreactor 61, properties such as a heat capacity and a thermal conductivity of metal to be used, the size of the microchannel portion 63, 65 to be formed, and so forth. For example, it can be set within a range of about 400 to 1000 $\mu$ m.

The microchannel portion 63, 65 of the metal substrate 62, 64 can be the same as the microchannel portion 43, 45 of the foregoing third embodiment.

[0032]

The formation of the metal oxide film 67 by the boehmite treatment in the flow path 66 of the joined body 75 formed by joining together the metal substrates 62 and 64 can be carried out according to the boehmite treatment for the joined body 35 in the foregoing second embodiment. The metal oxide film 67 formed by the boehmite treatment is an aluminum oxide thin film, and the thickness thereof can

be set within a range of, for example, about 0.5 to 5.0 $\mu$ m.

The insulating film 71 formed on the surface 62b of the metal substrate 62 can be the same as the insulating film 30 in the foregoing second embodiment.

Further, the catalyst C, the heater 68, the electrodes 69 and 69, and the heater protective layer 70 forming the microreactor 21 can be the same as the catalyst C, the heater 7, the electrodes 8 and 8, and the heater protective layer 9 forming the microreactor 1 in the foregoing first embodiment, respectively, and therefore, description thereof is omitted herein.

[0033]

In the microreactor 41, 61 of the present invention as described above, since the catalyst C is supported on the whole inner wall surface of the flow path 46, 66, the reaction area is increased to thereby obtain a high reaction efficiency. Further, use is made of the metal substrates 42 and 44, 62 and 64 each having a higher thermal conductivity and a smaller heat capacity as compared with a silicon substrate or a ceramic substrate, and therefore, heat is transmitted from the heater 48, 68 to the supported catalyst C with a high efficiency, so that there is enabled a reformer for hydrogen production wherein the rising is fast upon starting up from the stopped state and the utilization efficiency of the input power to the heater is high.

The foregoing embodiments of the microreactors are

only examples. For example, the positions of the feed material inlet and the gas outlet can be set to desirable positions by changing the shapes of the microchannel portions.

[0034]

#### Production Method of Microreactor

##### (First Embodiment)

Figs. 9 and 10 are process diagrams for describing one embodiment of the microreactor producing method of the present invention.

In Figs. 9 and 10, description will be made using the foregoing microreactor 1 as an example.

In the production method of the present invention, at the outset, in a channel portion forming process, a microchannel portion 3 is formed on one surface 2a of a metal substrate 2 (Fig. 9(A)). This microchannel portion 3 can be formed by forming a resist having a predetermined opening pattern on the surface 2a of the metal substrate 2, and etching the metal substrate 2 to leave comb-shaped ribs 2A and 2B by wet etching using the resist as a mask, which can make processing by a micromachine unnecessary. The microchannel portion 3 that is formed preferably has a circular arc shape, a semicircular shape, or a U-shape in section, and preferably has no angular portion on the wall surface along the fluid flow direction. With such a shape, it is possible to prevent a catalyst from being accumulated at angular portions in a later catalyst applying process so

that uniform catalyst applying is enabled. As a material of the metal substrate 2 that is used, there can be cited Al, Si, Ta, Nb, V, Bi, Y, W, Mo, Zr, Hf, or the like which enables formation of a metal oxide film by anodic oxidation in a subsequent surface treatment process.

[0035]

Then, in a joining process, a metal cover member 4 is joined to the metal substrate surface 2a to form a joined body 15 (Fig. 9(B)). As a material of the metal cover member 4, it is also possible to use Al, Si, Ta, Nb, V, Bi, Y, W, Mo, Zr, Hf, or the like which enables formation of a metal oxide film by anodic oxidation in the next surface treatment process. The joining of the metal cover member 4 to the metal substrate surface 2a can be implemented by, for example, diffusion bonding, or the like. Upon the joining, positioning is carried out so that a feed material inlet 4a and a gas outlet 4b provided in the cover member 4 coincide with both end portions of a flow path of the microchannel portion 3 formed on the metal substrate 2. In the joined body 15 thus formed, the microchannel portion 3 is covered with the metal cover member 4 to form a flow path 5.

Then, in the surface treatment process, the joined body 15 is anodically oxidized to form a metal oxide film (insulating film) 6 on the whole surfaces including an inner wall surface of the flow path 5 (Fig. 9(C)). The formation of this metal oxide film (insulating film) 6 can

be implemented by, in the state where the joined body 15 is connected to an anode as an external electrode, immersing the joined body 15 in an anode oxidizing solution so as to confront a cathode and energizing it.

[0036]

Then, in the catalyst applying process, a catalyst C is applied to the whole inner wall surface of the flow path 5 via the metal oxide film (insulating film) 6 (Fig. 10(A)). The applying of the catalyst C onto the metal oxide film (insulating film) 6 can be carried out by, for example, pouring a catalyst suspension into the flow path 5 of the joined body 15 to fill it, or immersing the joined body 15 in the catalyst suspension, and thereafter, removing the catalyst suspension from the flow path 5, and drying the joined body 15. In this catalyst applying process, as described above, when the sectional shape of the microchannel portion 3 is a circular arc shape, a semicircular shape, or a U-shape and no angular portion exists on the wall surface along the fluid flow direction, there exist hardly any angular portions, where the catalyst tends to be accumulated, within the flow path 5 so that uniform catalyst applying is enabled. Incidentally, by giving vibration or rotation to the joined body 15 upon the foregoing drying, more uniform catalyst applying is made possible.

[0037]

Then, a heater 7 is provided on the metal oxide

film (insulating film) 6 on the side of a surface 2b of the metal substrate 2, and further, electrodes 8 and 8 for energization are formed (Fig. 10(B)). The heater 7 can be formed using a material such as carbon paste, nichrome (Ni-Cr alloy), W, or Mo. As a method of forming the heater 7, there can be cited a method of forming it by screen printing using a paste containing the foregoing material, a method of forming an applied film using a paste containing the foregoing material, then patterning it by etching or the like, a method of forming a thin film by the vacuum deposition method using the foregoing material, then patterning it by etching or the like, or another.

[0038]

On the other hand, the electrodes 8 and 8 for energization can be formed using a conductive material such as Au, Ag, Pd, or Pd-Ag. For example, they can be formed by screen printing using a paste containing the foregoing conductive material.

Then, a heater protective layer 9 is formed on the heater 7 so as to expose the electrodes 8 and 8 (Fig. 10(C)). The heater protective layer 9 can be formed using a material such as polyimide or ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ). For example, it can be formed in a pattern having electrode opening portions 9a and 9a by screen printing using a paste containing the foregoing material.

[0039]

(Second Embodiment)

Figs. 11 and 12 are process diagrams for describing another embodiment of the microreactor producing method of the present invention.

In Figs. 11 and 12, description will be made using the foregoing microreactor 21 as an example.

In the production method of the present invention, at the outset, in a channel portion forming process, a microchannel portion 23 is formed on one surface 22a of a metal substrate 22 (Fig. 11(A)). For the metal substrate 22 that is used, it is possible to use a material such as Cu, stainless, Fe, or Al which enables formation of a metal oxide film by a boehmite treatment in a later surface treatment process. The formation of the microchannel portion 23 can be implemented like the formation of the microchannel portion 3 on the metal plate 2 in the foregoing embodiment.

[0040]

Then, in a joining process, after forming an insulating film 30 on a surface 22b, where the microchannel portion 23 is not formed, of the metal substrate 22, a metal cover member 24 is joined to the metal substrate surface 22a where the microchannel portion 23 is formed, to thereby form a joined body 35 (Fig. 11(B)).

The insulating film 30 can be formed using, for example, polyimide, ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ), or the like. The formation of the insulating film 30 can be implemented, for example, by the printing method such as screen printing

using a paste containing the foregoing insulating material, or by forming a thin film by the vacuum film forming method such as sputtering or vacuum deposition using the foregoing insulating material and curing it. Incidentally, the formation of the insulating film 30 may be carried out after the joining between the metal substrate 22 and the metal cover member 24.

[0041]

As a material of the metal cover member 24, it is possible to use a material such as Cu, stainless, Fe, or Al which enables formation of a metal oxide film by a boehmite treatment in the next surface treatment process. The joining of the metal cover member 24 to the metal substrate surface 22a can be implemented by, for example, diffusion bonding, or the like. Upon the joining, positioning is carried out so that a feed material inlet 24a and a gas outlet 24b provided in the metal cover member 24 coincide with both end portions of a flow path of the microchannel portion 23 formed on the metal substrate 22. In the joined body 35 thus formed, the microchannel portion 23 is covered with the metal cover member 24 to form a flow path 25.

Then, in the surface treatment process, a metal oxide film 26 is formed on an inner wall surface of the flow path 25 of the joined body 35 (Fig. 11(C)). The formation of the metal oxide film 26 can be implemented by the boehmite treatment. For example, it can be implemented by using a suspension with boehmite alumina such as alumina

sol being dispersed therein, and pouring the suspension with a fully lowered viscosity into the flow path 25, thereafter, drying it to fix a boehmite coating on the inner surface of the flow path (washcoat process).

[0042]

Then, in a catalyst applying process, a catalyst C is applied to the whole inner wall surface of the flow path 25 via the metal oxide film 26 (Fig. 12(A)). The applying of the catalyst C onto the metal oxide film 26 can be carried out like the catalyst applying process in the foregoing embodiment. Also in this embodiment, when the sectional shape of the microchannel portion 23 is a circular arc shape, a semicircular shape, or a U-shape and no angular portion exists on the wall surface along the fluid flow direction, there exist hardly any angular portions, where the catalyst tends to be accumulated, within the flow path 25 so that uniform catalyst applying is enabled. Incidentally, by giving vibration or rotation to the joined body 35 upon drying, more uniform catalyst applying is made possible.

Then, a heater 27 is provided on the insulating film 30 on the side of a surface 22b of the metal substrate 22, and further, electrodes 28 and 28 for energization are formed (Fig. 12(B)). Thereafter, a heater protective layer 29 is formed on the heater 27 so as to expose the electrodes 28 and 28 (Fig. 12(C)). Materials and forming methods of the heater 27, the electrodes 28 and 28, and the

heater protective layer 29 can be the same as in the foregoing embodiment.

[0043]

(Third Embodiment)

Figs. 13 and 14 are process diagrams for describing another embodiment of the microreactor producing method of the present invention.

In Figs. 13 and 14, description will be made using the foregoing microreactor 41 as an example.

In the production method of the present invention, at the outset, in a channel portion forming process, a microchannel portion 43 is formed on one surface 42a of a metal substrate 42, and a microchannel portion 45 is formed on one surface 44a of a metal substrate 44 (Fig. 13(A)). The microchannel portion 43, 45 can be formed by forming a resist having a predetermined opening pattern on the surface 42a, 44a of the metal substrate 42, 44 and etching the metal substrate 42, 44 to leave comb-shaped ribs 42A and 42B, 44A and 44B by wet etching using the resist as a mask, which can make processing by a micromachine unnecessary.

[0044]

The metal substrates 42 and 44 form a pair of metal substrates wherein pattern shapes of the microchannel portion 43 and the microchannel portion 45 that are formed have a symmetrical relationship with respect to a joining plane (42a, 44a) between the metal substrates 42 and 44.

Further, the microchannel portion 43, 45 preferably has a circular arc shape, a semicircular shape, or a U-shape in section, and preferably has no angular portion on the wall surface along the fluid flow direction (a turnback portion at each of tip portions of the comb-shaped ribs 42A and 42B, 44A and 44B is rounded with no angular portion). With such a shape, it is possible to prevent a catalyst from being accumulated at angular portions in a later catalyst applying process so that uniform catalyst applying is enabled. As a material of the metal substrate 42, 44 that is used, there can be cited Al, Si, Ta, Nb, V, Bi, Y, W, Mo, Zr, Hf, or the like which enables formation of a metal oxide film by anodic oxidation in a subsequent surface treatment process.

[0045]

Then, in a joining process, the pair of metal substrates 42 and 44 are joined together at the surfaces 42a and 44a such that the microchannel portion 43 and the microchannel portion 45 confront each other, thereby to form a joined body 55 (Fig. 13(B)).

As described above, the microchannel portion 43 and the microchannel portion 45 have the pattern shapes that are in a symmetrical relationship with respect to the joining plane (42a, 44a) between the metal substrates 42 and 44. Therefore, by the joining between the metal substrates 42 and 44, the microchannel portion 43 and the microchannel portion 45 completely confront each other to

form a flow path 46. The shape of an inner wall surface of the flow path 46 is generally circular in a section perpendicular to a fluid flow direction of the flow path 46. The foregoing joining between the metal substrates 42 and 44 can be carried out by, for example, diffusion bonding, or the like.

Then, in the surface treatment process, the joined body 55 is anodically oxidized to form a metal oxide film (insulating film) 47 on the whole surfaces including the inner wall surface of the flow path 46 (Fig. 13(C)). The formation of this metal oxide film (insulating film) 47 can be implemented by, in the state where the joined body 55 is connected to an anode as an external electrode, immersing the joined body 55 in an anode oxidizing solution so as to confront a cathode and energizing it.

[0046]

Then, in the catalyst applying process, a catalyst C is applied to the whole inner wall surface of the flow path 46 via the metal oxide film (insulating film) 47 (Fig. 14(A)). The applying of the catalyst C to the metal oxide film (insulating film) 47 can be carried out by, for example, pouring a catalyst suspension into the flow path 46 of the joined body 55 to fill it, or immersing the joined body 55 in the catalyst suspension, and thereafter, removing the catalyst suspension from the flow path 46, and drying the joined body 55. In this catalyst applying process, as described above, when the sectional shape of

the microchannel portion 43, 45 is a circular arc shape, a semicircular shape, or a U-shape and no angular portion exists on the wall surface along the fluid flow direction, there exist hardly any angular portions, where the catalyst tends to be accumulated, within the flow path 46 so that uniform catalyst applying is enabled. Incidentally, by giving vibration or rotation to the joined body 55 upon the foregoing drying, more uniform catalyst applying is made possible.

[0047]

Then, a heater 48 is provided on the metal oxide film (insulating film) 47 on the side of a surface 42b of the metal substrate 42, and further, electrodes 49 and 49 for energization are formed (Fig. 14(B)). The heater 48 can be formed using a material such as carbon paste, nichrome (Ni-Cr alloy), W, or Mo. As a method of forming the heater 48, there can be cited a method of forming it by screen printing using a paste containing the foregoing material, a method of forming an applied film using a paste containing the foregoing material, then patterning it by etching or the like, a method of forming a thin film by the vacuum deposition method using the foregoing material, then patterning it by etching or the like, or another.

[0048]

On the other hand, the electrodes 49 and 49 for energization can be formed using a conductive material such as Au, Ag, Pd, or Pd-Ag. For example, they can be formed

by screen printing using a paste containing the foregoing conductive material.

Then, a heater protective layer 50 is formed on the heater 48 so as to expose the electrodes 49 and 49 (Fig. 14(C)). The heater protective layer 50 can be formed using a material such as polyimide or ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ). For example, it can be formed in a pattern having electrode opening portions 50a and 50a by screen printing using a paste containing the foregoing material.

[0049]

(Fourth Embodiment)

Figs. 15 and 16 are process diagrams for describing another embodiment of the microreactor producing method of the present invention.

In Figs. 15 and 16, description will be made using the foregoing microreactor 61 as an example.

In the production method of the present invention, at the outset, in a channel portion forming process, a microchannel portion 63 is formed on one surface 62a of a metal substrate 62, and a microchannel portion 65 is formed on one surface 64a of a metal substrate 64 (Fig. 15(A)). The formation of the microchannel portion 63, 65 can be implemented like the formation of the microchannel portion 43, 45 on the metal substrate 42, 44 in the foregoing third embodiment. For the metal substrate 62, 64 that is used, it is possible to use a material such as Cu, stainless, Fe, or Al which enables formation of a metal oxide film by a

boehmite treatment in a later surface treatment process.

[0050]

Then, in a joining process, after forming an insulating film 71 on a surface 62b, where the microchannel portion 63 is not formed, of the metal substrate 62, the pair of metal substrates 62 and 64 are joined together at the surfaces 62a and 64a such that the microchannel portion 63 and the microchannel portion 65 confront each other, thereby to form a joined body 75 (Fig. 15(B)).

The insulating film 71 can be formed using, for example, polyimide, ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ), or the like. The formation of the insulating film 71 can be implemented, for example, by the printing method such as screen printing using a paste containing the foregoing insulating material, or by forming a thin film by the vacuum film forming method such as sputtering or vacuum deposition using the foregoing insulating material and curing it. Incidentally, the formation of the insulating film 71 may be carried out after the joining between the metal substrates 62 and 64.

The joining of the foregoing metal substrates 62 and 64 can be implemented by, for example, diffusion bonding, or the like. In this joining, since the microchannel portion 63 and the microchannel portion 65 have pattern shapes that are in a symmetrical relationship with respect to a joining plane (62a, 64a) between the metal substrates 62 and 64, the microchannel portion 63 and the microchannel portion 65 completely confront each other

to form a flow path 66. The shape of an inner wall surface of the flow path 66 is generally circular in a section perpendicular to a fluid flow direction of the flow path 66. [0051]

Then, in the surface treatment process, a metal oxide film 67 is formed on an inner wall surface of the flow path 66 of the joined body 75 (Fig. 15(C)). The formation of the metal oxide film 67 can be implemented by the boehmite treatment. For example, it can be implemented by using a suspension with boehmite alumina such as alumina sol being dispersed therein, and pouring the suspension with a fully lowered viscosity into the flow path 66, thereafter, drying it to fix a boehmite coating on the inner surface of the flow path (washcoat process).

Then, in a catalyst applying process, a catalyst C is applied to the whole inner wall surface of the flow path 66 via the metal oxide film 67 (Fig. 16(A)). The applying of the catalyst C to the metal oxide film 67 can be carried out like the catalyst applying process in the foregoing third embodiment. Also in this embodiment, when the sectional shape of the microchannel portion 63, 65 is a circular arc shape, a semicircular shape, or a U-shape and no angular portion exists on the wall surface along the fluid flow direction, an angular portion, where the catalyst tends to be accumulated, does not exist within the flow path 66 so that uniform catalyst applying is enabled. Incidentally, by giving vibration or rotation to the joined

body 75 upon drying, more uniform catalyst applying is made possible.

[0052]

Then, a heater 68 is provided on the insulating film 71 on the side of a surface 62b of the metal substrate 62, and further, electrodes 69 and 69 for energization are formed (Fig. 16(B)). Thereafter, a heater protective layer 70 is formed on the heater 68 so as to expose the electrodes 69 and 69 (Fig. 16(C)). Materials and forming methods of the heater 68, the electrodes 69 and 69, and the heater protective layer 70 can be the same as in the foregoing third embodiment.

[0053]

In the microreactor producing method of the present invention as described above, since the catalyst is applied after the joined body having the flow path therein is formed in the joining process, there is no possibility of deactivation of the catalyst due to heat in the joining process so that the selection width of the catalyst is broadened. Further, by preparing a plurality of joined bodies through completion up to the joining process and applying desired catalysts in these joined bodies, it is possible to produce microreactors to be used in different reactions, for example, microreactors for reforming methanol and for oxidation of carbon monoxide, and therefore, simplification of the production processes is made possible. Further, since the metal substrate is used,

the formation of the microchannel portion does not require the micromachine processing, but can be easily implemented by a low-priced processing method such as etching, and further, the polishing process is also unnecessary, so that reduction in production cost of the microreactor can be achieved. Further, if it is configured such that no angular portion exists on the inner wall surface of the flow path, dispersion of the applying amount in the catalyst applying process is suppressed so that the catalyst can be uniformly applied.

The foregoing embodiments of the microreactor producing methods are only examples, and the present invention is not limited thereto.

[EXAMPLE]

[0054]

Now, the present invention will be described in further detail showing more specific examples.

[Example 1]

An Al substrate (250mm x 250mm) having a thickness of 1000 $\mu$ m was prepared as a metal substrate, and a photosensitive resist material (OFPR produced by Tokyo Ohka Kogyo Co., Ltd.) was applied (film thickness 7 $\mu$ m (dried)) to both surfaces of the Al substrate by the dip method. Then, on the resist film on the side, where a microchannel portion was to be formed, of the Al substrate, there was disposed a photomask having a shape in which stripe-shaped light-shielding portions each having a width of 1500 $\mu$ m

projected (projecting length 30mm) alternately from right and left at pitches of 2000 $\mu$ m. In this photomask, a portion where each of the foregoing stripe-shaped light-shielding portions projected from a base portion did not form an angle of 90°, but formed an R-shape with a radius of 1750 $\mu$ m. Then, the resist film was exposed via the photomask and developed using a sodium bicarbonate solution. As a result, on one surface of the Al substrate, there was formed a resist pattern in which stripe-shaped opening portions each having a width of 500 $\mu$ m were arrayed at pitches of 2000 $\mu$ m, and the adjacent stripe-shaped opening portions were alternately continuous with each other at their end portions.

[0055]

Then, using the foregoing resist pattern as a mask, the Al substrate was subjected to etching (3 minutes) under the following condition.

(Etching Condition)

- Temperature : 20°C
- Etching Liquid (HCl) Concentration : 200g/L  
(one liter containing pure water and  
200g of 35% HCl dissolved therein)

[0056]

After the foregoing etching process was finished, the resist pattern was removed using a sodium hydroxide solution and washing was carried out. As a result, on the one surface of the Al substrate, there was formed a

microchannel portion (flow path length 300mm) having a shape wherein stripe-shaped microchannels each having a width of 1000 $\mu$ m, a depth of 650 $\mu$ m, and a length of 30mm were formed at pitches of 2000 $\mu$ m so as to be alternately continuous with each other at end portions of the adjacent microchannels (the shape continuously meandering while turning back by 180 degrees, as shown in Fig. 3). Turnback portions of the microchannel portion each had roundness with no angular portion, and no angular portion existed on an inner wall surface along a fluid flow direction. Further, the shape of the inner wall surface of the microchannel portion was generally semicircular in a section perpendicular to the fluid flow direction.

[0057]

Then, an Al plate having a thickness of 100 $\mu$ m was prepared as a metal cover member. This Al plate was diffusion bonded to the Al substrate formed with the microchannel portion as described above so as to cover the microchannel portion under the following condition, to thereby produce a joined body. This Al plate was provided with two opening portions (a feed material inlet and a gas outlet: size of each opening portion 0.6mm x 0.6mm), and positioning was carried out so that the opening portions coincided with both end portions of a flow path of the microchannel portion formed on the Al substrate. Consequently, the flow path connecting between the feed material inlet and the gas outlet was formed within the

joined body.

(Diffusion Bonding Condition)

- Atmosphere : Under Vacuum
- Bonding Temperature : 300°C
- Bonding Time : 8 Hours

[0058]

Then, the foregoing joined body was connected to an anode as an external electrode, immersed in an anode oxidizing solution (4% oxalic acid solution) so as to confront a cathode, and energized under the following condition, to thereby form an aluminum oxide thin film, serving as an insulating film, on the surfaces of the joined body including the inside of the flow path. The thickness of the formed aluminum oxide thin film was measured by an ellipsometer, and the result was about 30 $\mu$ m.

(Anodic Oxidation Condition)

- Bath Temperature : 25°C
- Voltage : 25V (DC)
- Current Density : 100A/m<sup>2</sup>

[0059]

Then, a catalyst suspension having the following composition was filled into the flow path of the joined body and left standing (15 minutes). Then, the catalyst suspension was removed, and a dry/reduction treatment was carried out at 120°C for three hours to thereby apply a catalyst over the whole surface within the flow path.

(Composition of Catalyst Suspension)

· Al	... 41.2 weight%
· Cu	... 2.6 weight%
· Zn	... 2.8 weight%

[0060]

Then, on the aluminum oxide thin film, where the microchannel portion was not formed, of the Al substrate, a paste for heater having the following composition was printed by screen printing, and then cured at 200°C to form a heater. The formed heater had a shape in which a fine line having a width of 100μm was drawn around on the Al substrate at line intervals of 100μm so as to cover the whole of a region (35mm x 25mm) corresponding to a region where the microchannel portion was formed.

(Composition of Paste for Heater)

· Carbon Powder	... 20 weight parts
· Fine Powder Silica	... 25 weight parts
· Xylene Phenol Resin	... 36 weight parts
· Butyl Carbitol	... 19 weight parts

[0061]

Further, using a paste for electrode having the following composition, electrodes (0.5mm x 0.5mm) were formed at predetermined two portions of the heater by screen printing.

(Composition of Paste for Electrode)

· Silver-plated Copper Powder	... 90 weight parts
· Phenol Resin	... 6.5 weight parts
· Butyl Carbitol	... 3.5 weight parts

[0062]

Then, using a paste for protective layer having the following composition, a heater protective layer (thickness 20 $\mu$ m) was formed on the heater by screen printing so as to expose the two electrodes formed on the heater.

(Composition of Paste for Protective Layer)

· Resin Concentration	...	30 weight parts
· Silica Filler	...	10 weight parts
· Lactone Solvent	...	60 weight parts

(penta-1, 4-lactone)

Consequently, a microreactor of the present invention was obtained.

[0063]

[Example 2]

An Al substrate (250mm x 250mm) having a thickness of 1000 $\mu$ m was prepared as a metal substrate, and a photosensitive resist material (OFPR produced by Tokyo Ohka Kogyo Co., Ltd.) was applied (film thickness 7 $\mu$ m (dried)) to both surfaces of the Al substrate by the dip method. Then, on the resist film on the side, where a microchannel portion was to be formed, of the Al substrate, there was disposed a photomask having a shape in which stripe-shaped light-shielding portions each having a width of 1500 $\mu$ m projected (projecting length 30mm) alternately from right and left at pitches of 2000 $\mu$ m. In this photomask, a portion where each of the foregoing stripe-shaped light-

shielding portions projected from a base portion did not form an angle of  $90^\circ$ , but formed an R-shape with a radius of  $1750\mu\text{m}$ . The same Al substrate as described above was prepared, the photosensitive resist material was applied in the same manner, and a photomask was disposed on the resist film on the side, where a microchannel portion was to be formed, of the Al substrate. This photomask was configured to be plane-symmetrical with the foregoing photomask with respect to the Al substrate surface.

[0064]

Then, with respect to the foregoing pair of metal substrates, the resist films were exposed via the photomasks, respectively, and developed using a sodium bicarbonate solution. As a result, on one surface of each Al substrate, there was formed a resist pattern in which stripe-shaped opening portions each having a width of  $500\mu\text{m}$  were arrayed at pitches of  $2000\mu\text{m}$ , and the adjacent stripe-shaped opening portions were alternately continuous with each other at their end portions.

[0065]

Then, using the foregoing resist pattern as a mask, the Al substrate was subjected to etching (3 minutes) under the following condition.

(Etching Condition)

- Temperature :  $20^\circ\text{C}$
- Etching Liquid (HCl) Concentration :  $200\text{g/L}$   
(one liter containing pure water and

200g of 35% HCl dissolved therein)

[0066]

After the foregoing etching process was finished, the resist pattern was removed using a sodium hydroxide solution and washing was carried out. As a result, on the one surface of each of the pair of Al substrates, there was formed a microchannel portion (flow path length 300mm) having a shape wherein stripe-shaped microchannels each having a width of 1000 $\mu$ m, a depth of 650 $\mu$ m, and a length of 30mm were formed at pitches of 2000 $\mu$ m so as to be alternately continuous with each other at end portions of the adjacent microchannels (the shape continuously meandering while turning back by 180 degrees, as shown in Fig. 7). Turnback portions of the microchannel portion each had roundness with no angular portion, and no angular portion existed on an inner wall surface along a fluid flow direction. Further, the shape of the inner wall surface of the microchannel portion was generally semicircular in a section perpendicular to the fluid flow direction.

[0067]

Then, the foregoing pair of Al substrates were diffusion bonded together under the following condition so that the mutual microchannel portions confront each other, thereby producing a joined body. Upon this bonding, positioning was carried out so that the microchannel portions of the pair of Al substrates completely confront each other. Consequently, within the joined body, there

was formed a flow path having a feed material inlet and a gas outlet that are located at one end surface of the joined body.

(Diffusion Bonding Condition)

- Atmosphere : Under Vacuum
- Bonding Temperature : 300°C
- Bonding Time : 8 Hours

[0068]

Then, the foregoing joined body was connected to an anode as an external electrode, immersed in an anode oxidizing solution (4% oxalic acid solution) so as to confront a cathode, and energized under the following condition, to thereby form an aluminum oxide thin film, serving as an insulating film, on the surfaces of the joined body including the inside of the flow path. The thickness of the formed aluminum oxide thin film was measured by an ellipsometer, and the result was about 30 $\mu$ m.

(Anodic Oxidation Condition)

- Bath Temperature : 25°C
- Voltage : 25V (DC)
- Current Density : 100A/m<sup>2</sup>

[0069]

Then, a catalyst suspension having the following composition was filled into the flow path of the joined body and left standing (15 minutes). Then, the catalyst suspension was removed, and a dry/reduction treatment was carried out at 120°C for three hours to thereby apply a

catalyst over the whole surface within the flow path.

(Composition of Catalyst Suspension)

· Al	...	41.2 weight%
· Cu	...	2.6 weight%
· Zn	...	2.8 weight%

Then, a heater, electrodes, and a heater protective layer were formed, like in Example 1, on the aluminum oxide thin film of one of the Al substrates.

Consequently, a microreactor of the present invention was obtained.

[0070]

[Example 3]

A SUS304 substrate (250mm x 250mm) having a thickness of 1000 $\mu$ m was prepared as a metal substrate, and a photosensitive resist material (OFPR produced by Tokyo Ohka Kogyo Co., Ltd.) was applied (film thickness 7 $\mu$ m (dried)) to both surfaces of the SUS304 substrate by the dip method. Then, on the resist film on the side, where a microchannel portion was to be formed, of the SUS304 substrate, there was disposed a photomask having a shape in which stripe-shaped light-shielding portions each having a width of 1500 $\mu$ m projected (projecting length 30mm) alternately from right and left at pitches of 2000 $\mu$ m. In this photomask, a portion where each of the foregoing stripe-shaped light-shielding portions projected from a base portion did not form an angle of 90°, but formed an R-shape with a radius of 1750 $\mu$ m. The same SUS304 substrate

as described above was prepared, the photosensitive resist material was applied in the same manner, and a photomask was disposed on the resist film on the side, where a microchannel portion was to be formed, of the SUS304 substrate. This photomask was configured to be plane-symmetrical with the foregoing photomask with respect to the SUS304 substrate surface.

[0071]

Then, with respect to the foregoing pair of metal substrates (SUS304 substrates), the resist films were exposed via the photomasks, respectively, and developed using a sodium bicarbonate solution. As a result, on one surface of each SUS304 substrate, there was formed a resist pattern in which stripe-shaped opening portions each having a width of 500 $\mu$ m were arrayed at pitches of 2000 $\mu$ m, and the adjacent stripe-shaped opening portions were alternately continuous with each other at their end portions.

Then, using the foregoing resist pattern as a mask, the SUS304 substrate was subjected to etching (3 minutes) under the following condition.

(Etching Condition)

- Temperature : 80°C
- Etching Liquid (ferric chloride solution)  
Specific Weight Concentration : 45 (° B'e)

[0072]

After the foregoing etching process was finished, the resist pattern was removed using a sodium hydroxide

solution and washing was carried out. As a result, on the one surface of each of the pair of SUS304 substrates, there was formed a microchannel portion (flow path length 300mm) having a shape wherein stripe-shaped microchannels each having a width of 1000 $\mu$ m, a depth of 650 $\mu$ m, and a length of 30mm were formed at pitches of 2000 $\mu$ m so as to be alternately continuous with each other at end portions of the adjacent microchannels (the shape continuously meandering while turning back by 180 degrees, as shown in Fig. 7). Turnback portions of the microchannel portion each had roundness with no angular portion, and no angular portion existed on an inner wall surface along a fluid flow direction. Further, the shape of the inner wall surface of the microchannel portion was generally semicircular in a section perpendicular to the fluid flow direction.

[0073]

Then, the pair of SUS304 substrates comprising this SUS304 substrate and the other SUS304 substrate were diffusion bonded together under the following condition so that the mutual microchannel portions confront each other, thereby producing a joined body. Upon this bonding, positioning was carried out so that the microchannel portions of the pair of SUS304 substrates completely confront each other. Consequently, within the joined body, there was formed a flow path having a feed material inlet and a gas outlet that are located at one end surface of the joined body.

(Diffusion Bonding Condition)

- Atmosphere : Under Vacuum
- Bonding Temperature : 1000°C
- Bonding Time : 12 Hours

[0074]

Then, on the surface, where the microchannel portion was not formed, of one of the SUS304 substrates forming the foregoing joined body, a polyimide precursor solution (Photoneece produced by Toray Industries, Inc.) as an application liquid for insulating film was printed by screen printing, then cured at 350°C to thereby form an insulating film having a thickness of 20 $\mu$ m.

Then, a boehmite treatment was applied to the inner wall surface of the flow path of the foregoing joined body under the following condition to form an aluminum oxide thin film. The thickness of the formed aluminum oxide thin film was measured by an ellipsometer, and the result was about 5 $\mu$ m.

(Condition of Boehmite Treatment)

Aluminasol 520 (produced by Nissan Chemical Industries, Ltd.) was used to prepare an alumina sol suspension with a viscosity of 15 to 20mPa·s. Then, this alumina sol suspension was poured into the flow path of the joined body, and drying was carried out at 120°C for three hours to thereby fix a boehmite film inside the flow path.

[0075]

Then, a catalyst was applied over the whole

surface in the flow path of the joined body like in Example 2. Thereafter, a heater, electrodes, and a heater protective layer were formed, like in Example 1, on the insulating film formed on one of the SUS304 substrates.

Consequently, a microreactor of the present invention was obtained.

[INDUSTRIAL APPLICATION]

[0076]

The present invention can be utilized for hydrogen production achieved from reactions such as reforming of methanol and oxidation of carbon monoxide.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0077]

Fig. 1 is a perspective view showing one embodiment of a microreactor of the present invention.

Fig. 2 is an enlarged longitudinal sectional view of the microreactor shown in Fig. 1, taken along line A-A.

Fig. 3 is a perspective view showing the side, where a microchannel portion is formed, of a metal substrate forming the microreactor shown in Fig. 1.

Fig. 4 is a longitudinal sectional view, corresponding to Fig. 2, showing another embodiment of a microreactor of the present invention.

Fig. 5 is a perspective view showing another embodiment of a microreactor of the present invention.

Fig. 6 is an enlarged longitudinal sectional view of the microreactor shown in Fig. 5, taken along line B-B.

Fig. 7 is a perspective view showing the side, where a microchannel portion is formed, of each of metal substrates forming the microreactor shown in Fig. 5.

Fig. 8 is a longitudinal sectional view, corresponding to Fig. 6, showing another embodiment of a microreactor of the present invention.

Fig. 9 is a process diagram for describing one embodiment of a microreactor producing method of the present invention.

Fig. 10 is a process diagram for describing one embodiment of a microreactor producing method of the present invention.

Fig. 11 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

Fig. 12 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

Fig. 13 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

Fig. 14 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

Fig. 15 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

Fig. 16 is a process diagram for describing another embodiment of a microreactor producing method of the present invention.

[DESCRIPTION OF THE REFERENCE NUMERALS]

[0078]

1,21,41,61	microreactor
2,22,42,44,62,64	metal substrate
3,23,43,45,63,65	microchannel portion
5,25,46,66	flow path
6,26,47,67	metal oxide film (insulating film)
30,71	insulating film
7,27,48,68	heater
8,28,49,69	electrode
9,29,50,70	heater protective layer
4,24	metal cover member
4a,24a,46a	material inlet
4b,24b,46b	gas outlet
C	catalyst

### Drawing

Fig.1

Fig.2





[Fig.7]

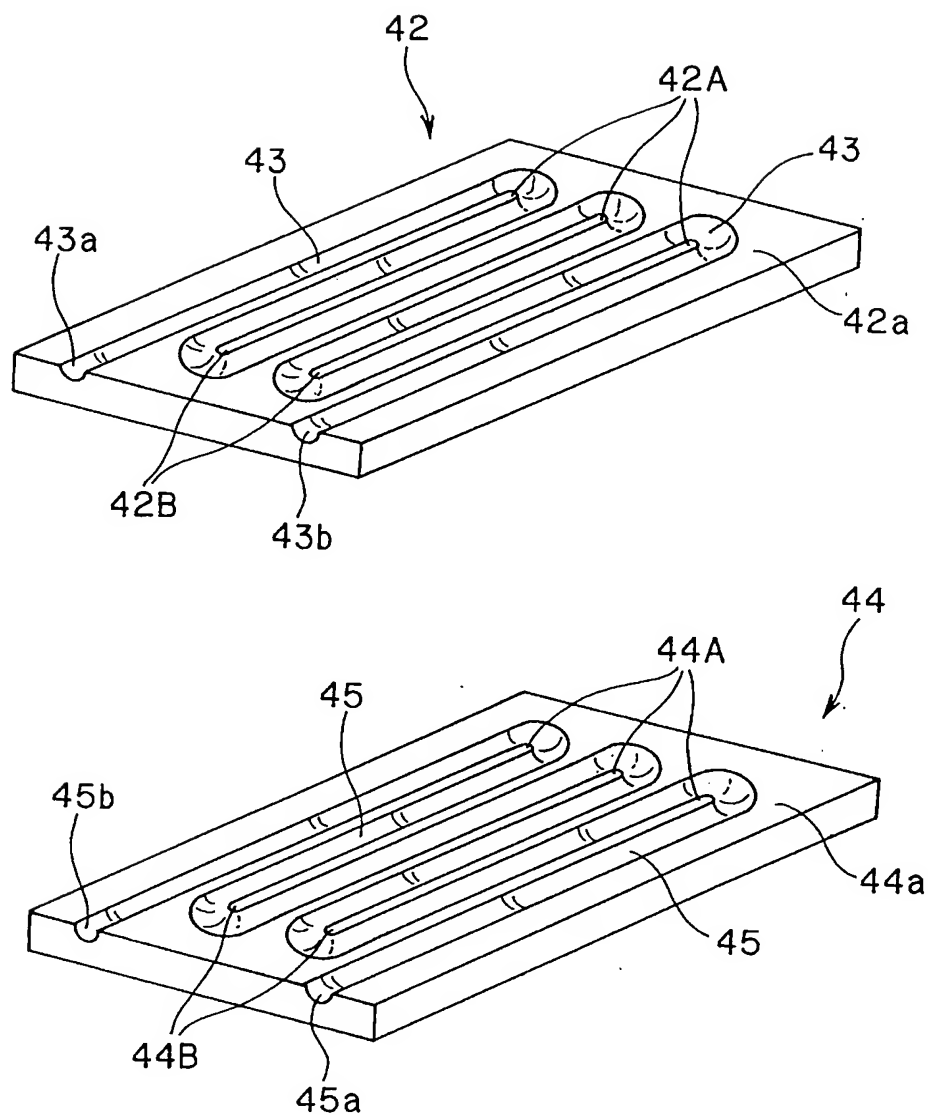


Fig.7

[Fig. 8]

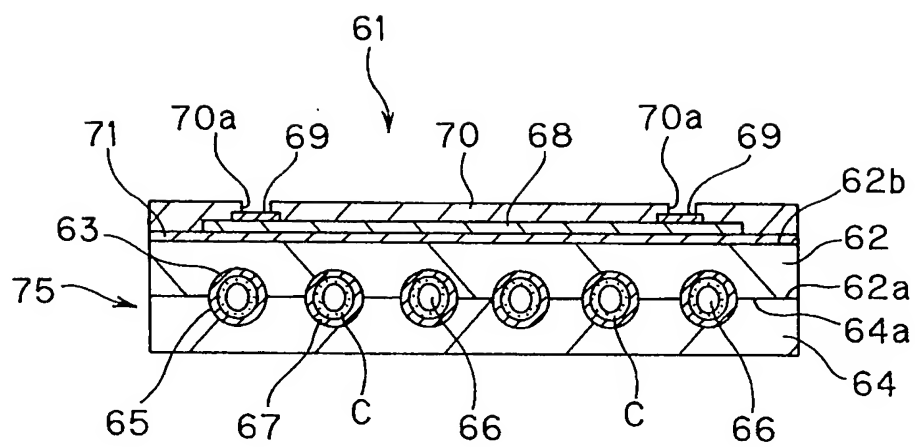


Fig.8

[Fig.9]

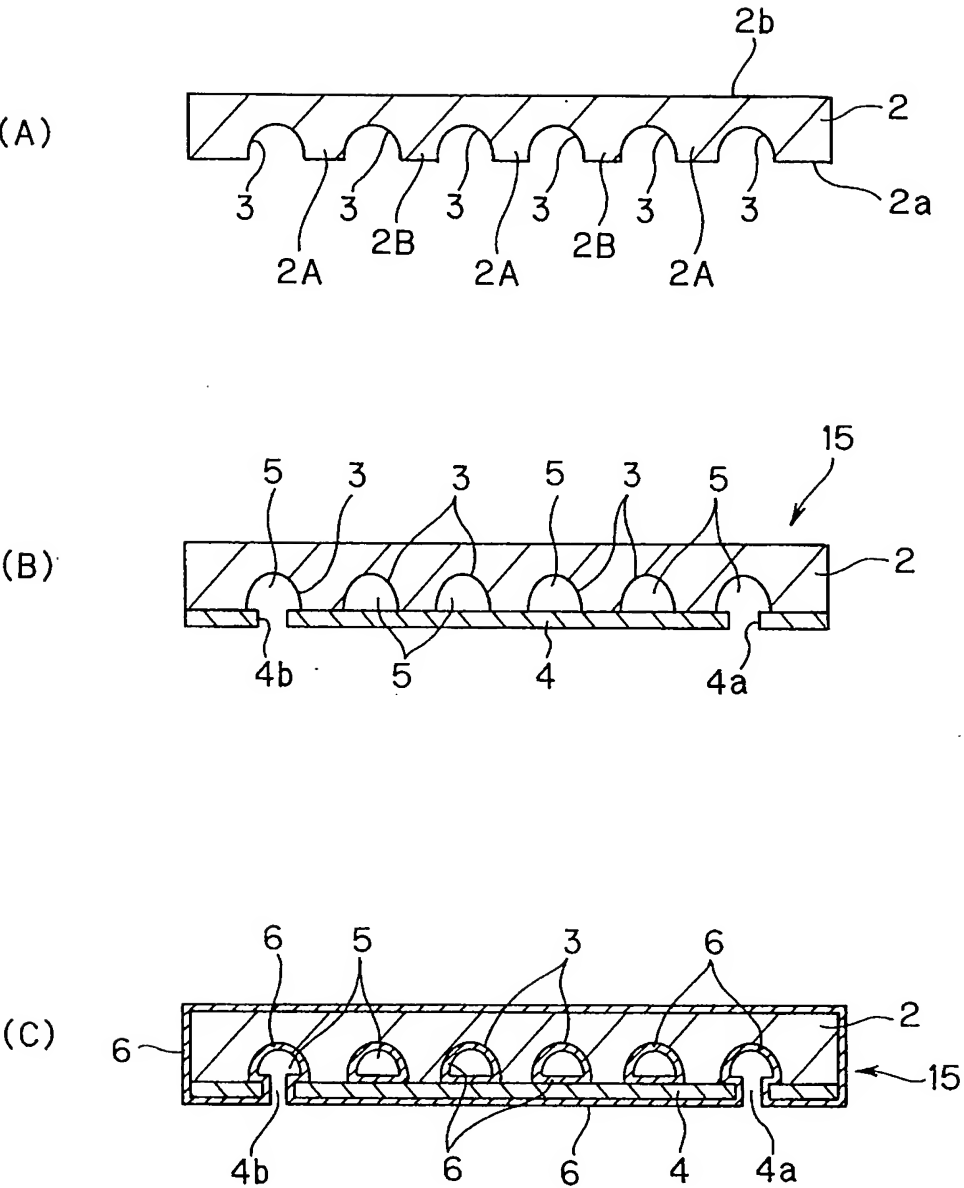


Fig.9

[Fig.10]

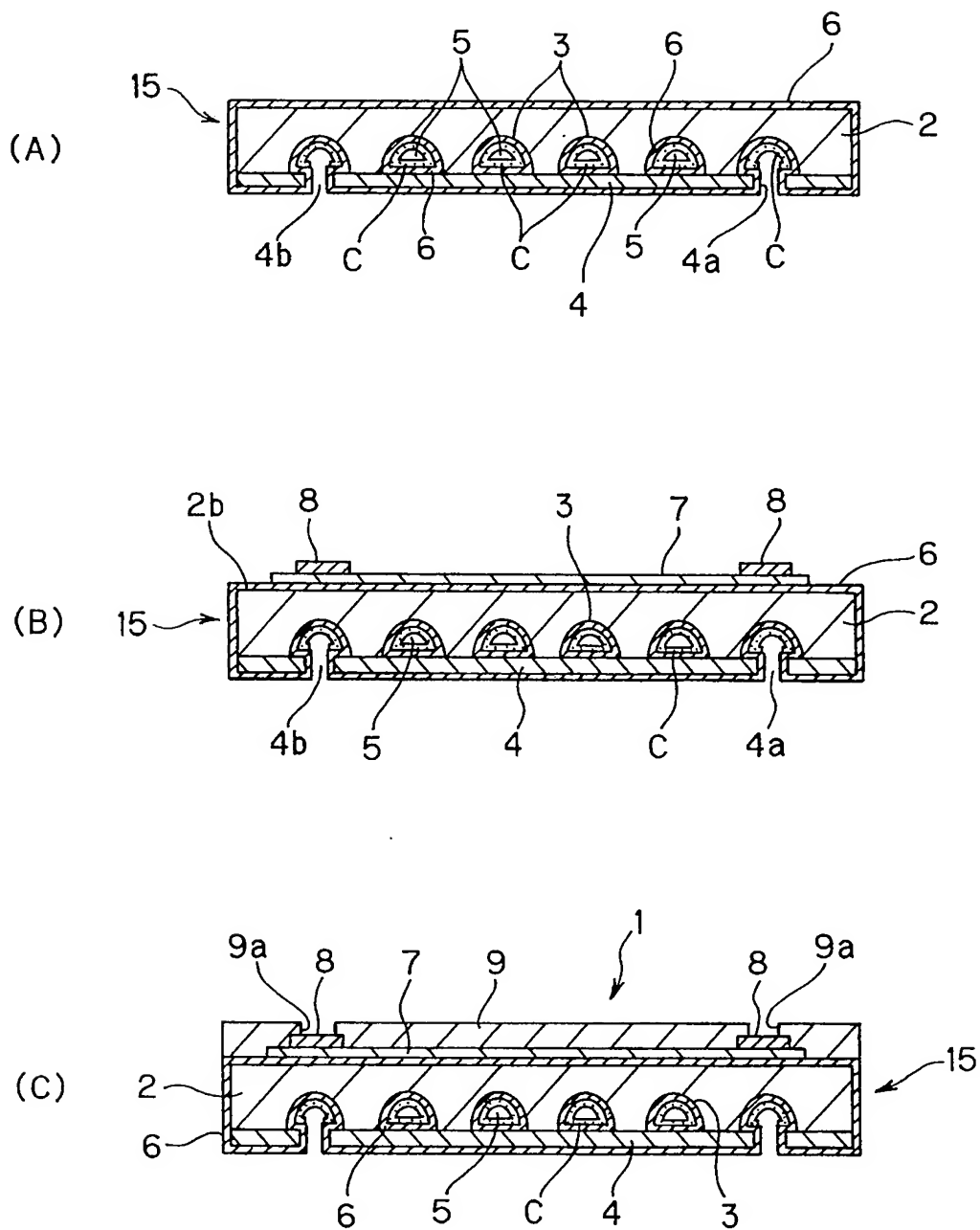


Fig.10

[Fig.11]

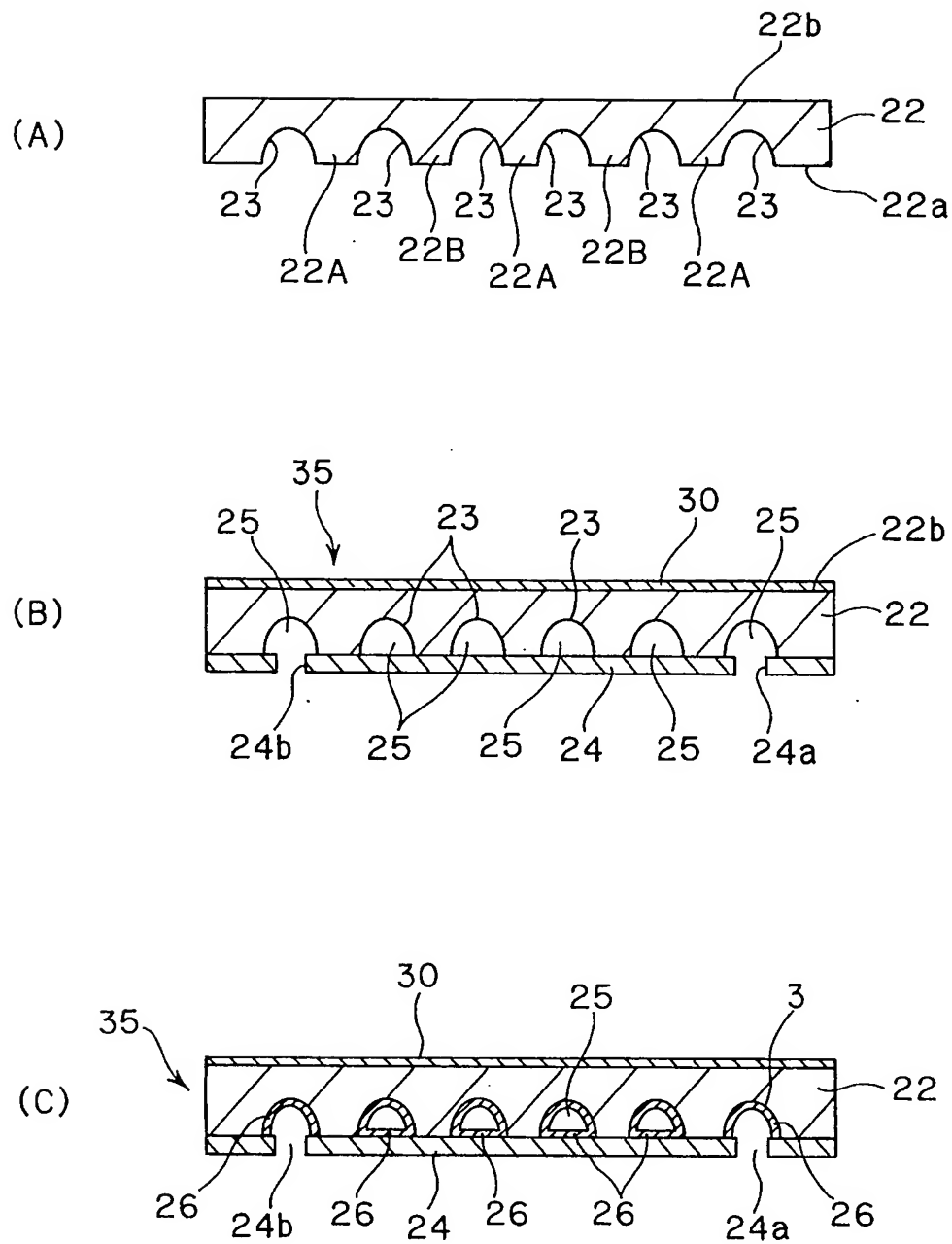


Fig.11

[Fig.12]

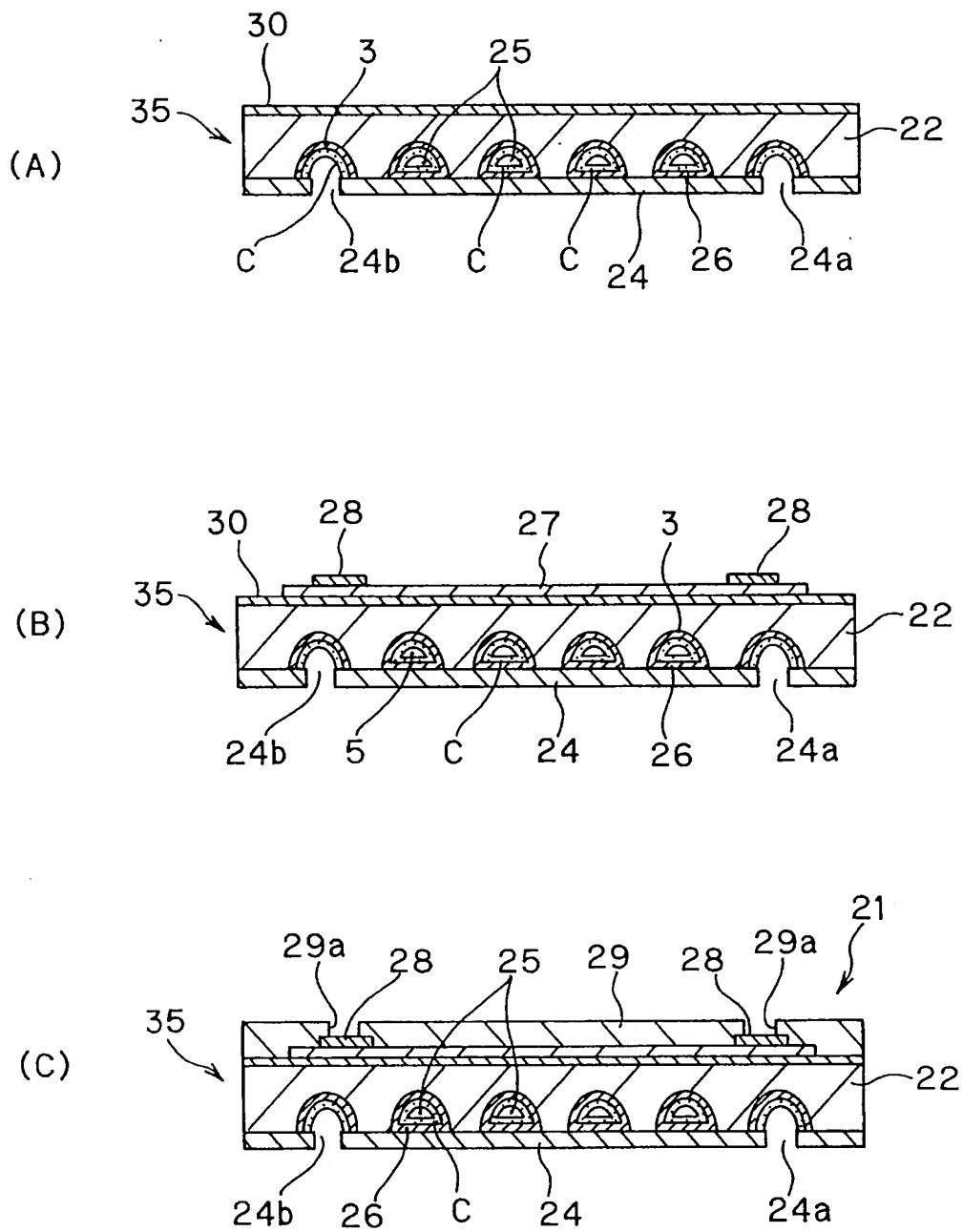


Fig.12

[Fig.13]

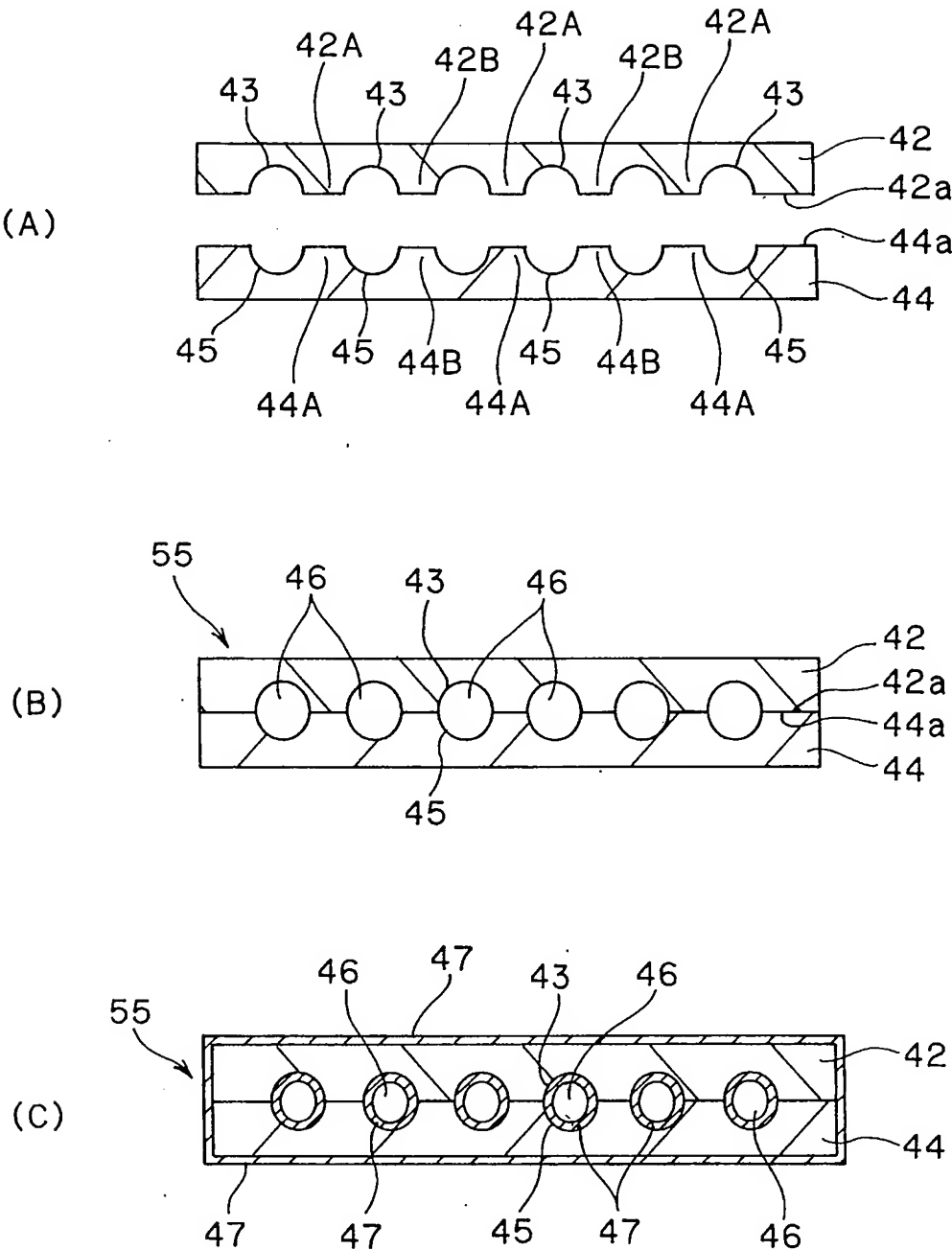


Fig.13

[Fig.14]

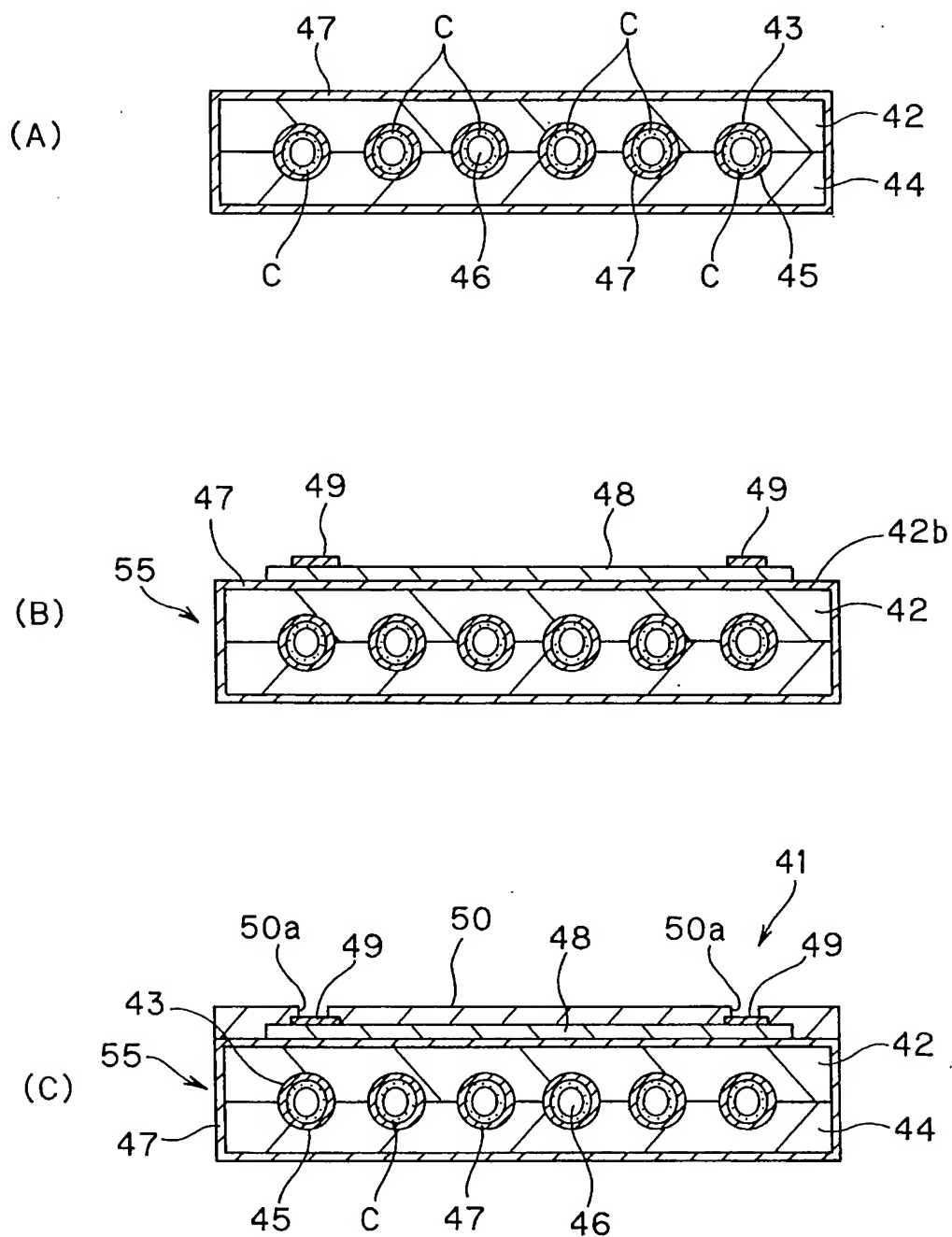


Fig.14

[Fig.15]

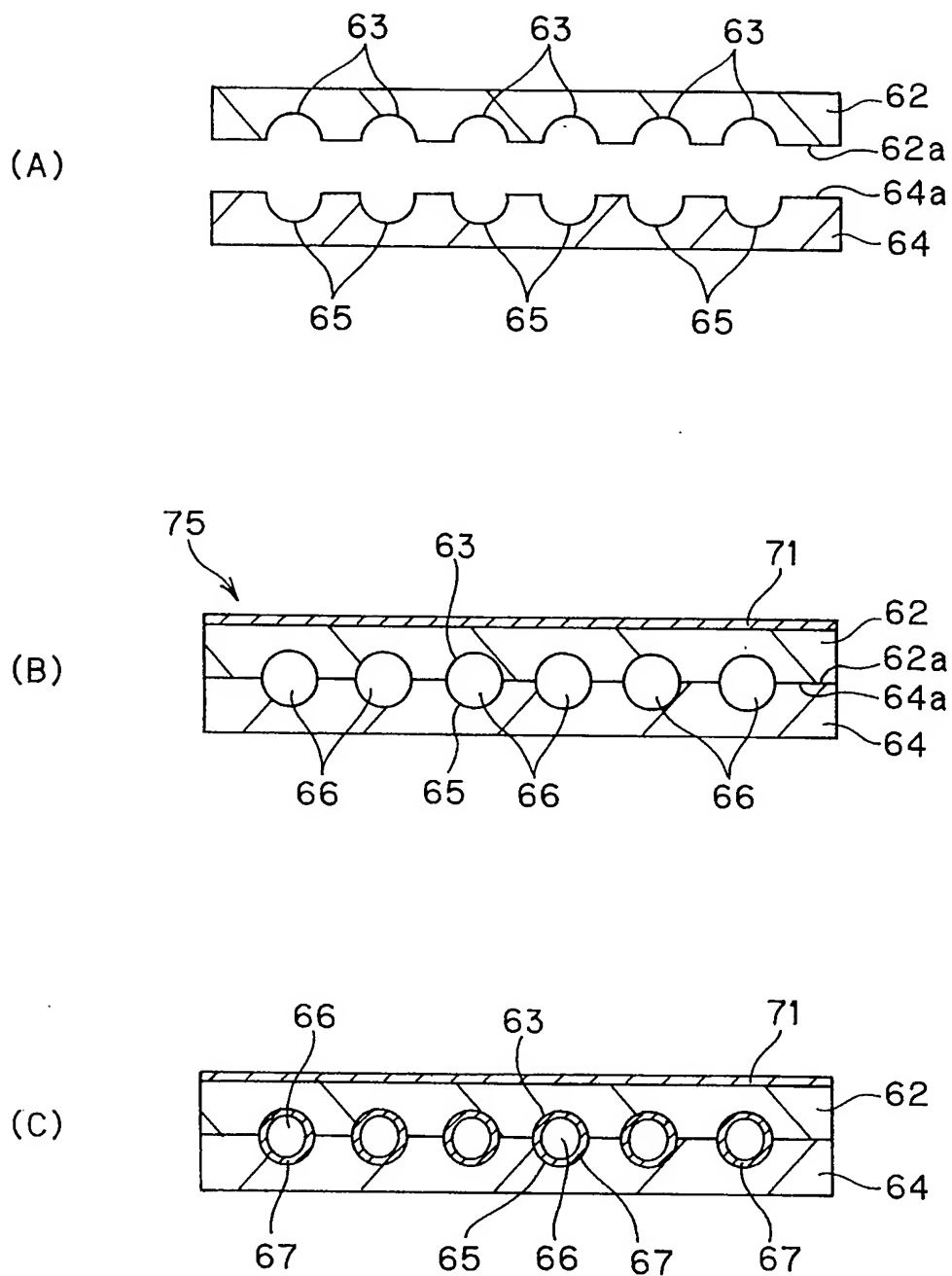


Fig.15

[Fig.16]

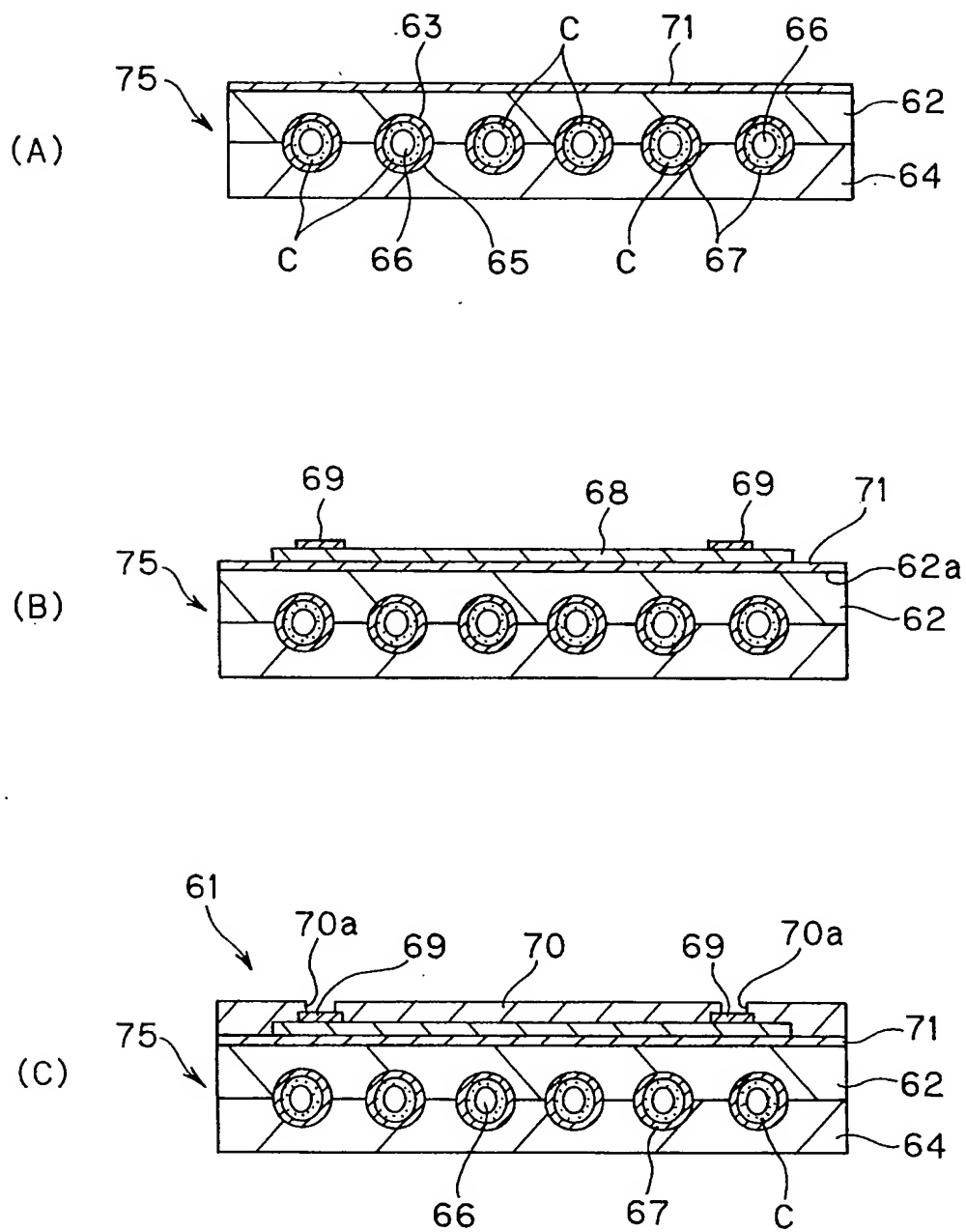


Fig.16

[NAME OF DOCUMENT]      Abstract

[ABSTRACT]

[PROBLEM]

To provide a microreactor that enables a small-sized and highly-efficient reformer for hydrogen production, and a production method that can easily produce such a microreactor.

[SOLVING MEANS]

A microreactor is configured to comprise a joined body formed by joining a metal cover member having a feed material inlet and a gas outlet to a metal substrate so as to cover a microchannel portion provided on one surface of the metal substrate, a flow path formed by the microchannel portion located inside the joined body, and a catalyst supported on a whole inner wall surface of the flow path. In the production of such a microreactor, the catalyst is applied to the flow path after forming the joined body.

[SELECTED DRAWING] Fig. 2